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# Pressure-induced transformation in NiTi-CuAg shape memory alloys: investigation of microstructural and thermodynamic changes

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## Abstract

Shape memory alloys (SMAs), particularly nickel-titanium (NiTi) based systems, are widely recognized for their unique shape memory effect and superelastic behavior, driven by reversible martensitic phase transformations. To enhance these functional properties for advanced applications, alloying with elements such as copper (Cu) and silver (Ag) has been explored. This study investigates the synthesis and characterization of a novel quaternary NiTiCuAg shape memory alloy. The alloy was fabricated via arc-melting from high-purity elemental powders, followed by application of varying uniaxial compressive pressures to assess their effects on phase transformation behavior. Thermal, structural, and microstructural properties were evaluated using Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy coupled with Energy-Dispersive x-ray Spectroscopy (SEM-EDX), and x-ray Diffraction (XRD). The results aim to elucidate the combined effects of compositional tailoring and mechanical processing on the functional performance of NiTiCuAg SMAs, with implications for their use in high-performance, pressure-sensitive applications.

## 1. Introduction

Shape memory alloys (SMAs) are a unique class of materials that can recover their original shape after deformation when exposed to specific thermal or mechanical stimuli [1]. Among these, nickel-titanium (NiTi) alloys, commonly known as Nitinol, have garnered significant attention due to their exceptional shape memory effect and superelasticity. These properties arise from a reversible martensitic transformation between the high-temperature austenite phase and the low-temperature martensite phase. Nitinol's remarkable attributes, including high damping capacity [2], corrosion resistance [3], and biocompatibility [4], have led to its widespread application in biomedical devices [5], actuators [6], and aerospace components [7]. Despite the superior properties of NiTi alloys, research continues to enhance their functional performance to meet the requirements of advanced engineering and biomedical applications. The most effective method to achieve this goal is alloying NiTi with additional components. Phase transformation temperatures, mechanical strength, and functional stability can be adjusted to the desired level using this method. The cyclic stability of the shape memory effect is a result of the copper (Cu) addition reducing the stability of the martensitic transformation and thermal hysteresis [8–10]. The addition of silver (Ag) increases mechanical strength and corrosion resistance while also imparting antibacterial properties. This is a significant advantage, particularly for biomedical implant and stent applications [11].

The addition of Cu and Ag to NiTi alloys not only alters their phase transformation properties but also affects microstructure and mechanical performance. The Cu addition improves martensitic transformation behavior by narrowing the transformation temperature range. Ag enhances compressive strength and

antibacterial properties while achieving these improvements without significantly compromising shape memory. Research in the literature shows that NiTi alloys with Ag additions exhibit both high compressive strength and maintain the desired transformation temperatures. Therefore, they are suitable material options for applications requiring mechanical strength and biocompatibility [12–15].

In this study, the synthesis and characterization of a quaternary  $\text{Ni}_{39}\text{Ti}_{49}\text{Cu}_8\text{Ag}_4$  (% at.) shape memory alloy were performed. Specifically, this study focused on investigating the effects of different uniaxial pressures on the phase transformation behavior and microstructural evolution of the alloy.  $\text{Ni}_{39}\text{Ti}_{49}\text{Cu}_8\text{Ag}_4$  (% at.) alloys produced in ingot form were subjected to different uniaxial pressures. This demonstrated that the phase transformation properties and structural changes are pressure-dependent. Differential Scanning Calorimetry (DSC) was used to determine the thermal properties of the alloy, Scanning Electron Microscopy-Energy Dispersive x-ray Spectroscopy (SEM-EDX) was used to examine the microstructure and distribution of elements, and x-ray Diffraction (XRD) was used for phase analysis. This systematic approach aims to contribute to the understanding of process-parameter-property relationships by detailing the effects of mechanical pressure on the structural and functional properties of the  $\text{Ni}_{39}\text{Ti}_{49}\text{Cu}_8\text{Ag}_4$  (in at.) alloy.

## 2. Material and methods

### 2.1. Materials

High-purity elemental powders of Nickel (Ni), Titanium (Ti), Copper (Cu), and Silver (Ag) with a purity of  $\geq 99.99\%$  were procured from Sigma-Aldrich. These powders were selected as the starting materials for the synthesis of the quaternary NiTiCuAg shape memory alloy (SMA). All materials were used without further purification.

### 2.2. Sample preparation

For the preparation of the alloy having the composition  $\text{Ni}_{39}\text{Ti}_{49}\text{Cu}_8\text{Ag}_4$  the required amounts of Ni, Ti, Cu, and Ag were calculated based on the target composition of the NiTiCuAg alloy and accurately weighed using a high-precision electronic analytical balance with a sensitivity of 0.1 mg. The powders were then thoroughly mixed to ensure homogeneity. After mixing, the powder mixture was cold-pressed into a pellet using a hydraulic press to improve handling and facilitate arc melting. The pellet was then subjected to arc melting in a water-cooled copper crucible under a high-purity argon atmosphere to prevent oxidation. The arc melting process was repeated three times with flipping between each melt to ensure chemical uniformity. The resulting alloy ingot was allowed to cool naturally to room temperature inside the arc melting chamber. The as-melted ingot was then sectioned into five equal parts using a cutting machine. These samples were each subjected to different amount uniaxial compressive pressures: 0 MPa, 100 MPa, 200 MPa, 300 MPa, and 400 MPa. The samples were labeled as S1, S2, S3, S4, and S5, respectively, corresponding to the applied pressure.

### 2.3. Characterization techniques

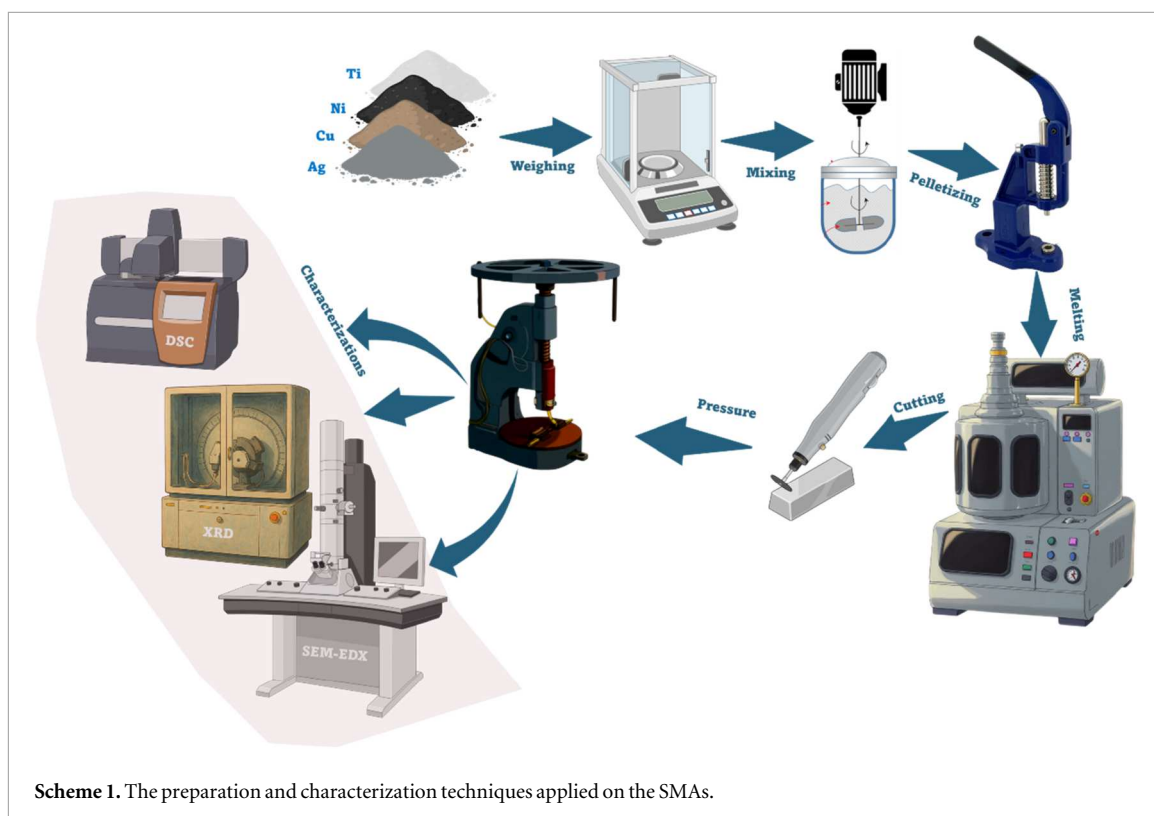
Phase transformation behavior of the alloy samples was investigated using a Differential Scanning Calorimeter (DSC). The measurements were performed in a nitrogen atmosphere at a heating and cooling rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of  $-50^\circ\text{C}$  to  $150^\circ\text{C}$ . This analysis aimed to determine the change of martensitic transformation temperatures and the thermal stability of the samples under different applied pressures. The microstructural features and elemental distribution of the samples were examined using Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive x-ray Spectroscopy (EDX). Prior to imaging, the samples were mechanically polished. EDX analysis was conducted to confirm the elemental composition and uniformity across the sample surfaces. Phase identification and structural analysis were carried out using x-ray Diffraction (XRD). The measurements were performed using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) over a  $2\theta$  range of  $20^\circ$ – $80^\circ$ , with a step size of  $2^\circ$ . The obtained diffraction patterns were analyzed using standard databases to identify crystalline phases and assess the effect of pressure on structural changes.

### 2.4. Synthesis workflow

A visual representation of the synthesis and characterization process is illustrated in Scheme 1, which outlines the sequence from raw material selection, alloy preparation, pressure treatment, and subsequent characterization.

## 3. Results and discussion

The x-ray patterns of the alloy subjected to different pressures are shown in figure 1(a). The x-ray diffraction patterns of the alloy were determined to be compatible with existing studies with the help of literature XRD



**Scheme 1.** The preparation and characterization techniques applied on the SMAs.

indexed by [16–18]. These detected peaks belong to the B2 (austenite, high temperature main phase peak, bcc crystal structure [19]) and B19 (martensite, low temperature product phase peak, orthorhombic crystal structure [19]) phases. Upon careful examination of figure 1(a), it can be seen that the S3 sample subjected to 200 MPa compression pressure has a distinctly sharper and more intense diffraction peak compared to the other samples. This increase in peak intensity and decrease in full width at half maximum (FWHM) indicate an increase in crystallinity and a decrease in lattice defects. This is due to structural improvement resulting from the rearrangement of the crystal lattice under high pressure. To better understand this evolution in the crystal structure, the crystallite grain sizes of the alloys were calculated using the Scherrer equation based on the FWHM values of the dominant diffraction peaks. This parameter also affects the mechanical properties of the alloys. The crystallite size of the alloys was estimated by the Scherrer equation (1) [20]:

$$D = K \lambda / (\beta \cos \theta) \quad (1)$$

where  $\lambda$ ,  $\theta$ ,  $\beta$ , and  $K$  are the x-ray monochromatic wavelength, diffraction angle, full width at half maximum (FWHM), and Scherrer's constant ( $\cong 0.9$ ). Figure 1(b) shows the crystallite size distribution of the alloys obtained from XRD peak broadening analysis. Each histogram represents the distribution of crystallite sizes calculated for the corresponding sample. The horizontal axis indicates the crystallite size (nm), while the vertical axis represents the number of crystallites (count). The crystallite size values were calculated from the full width at half maximum (FWHM) of the diffraction peaks using the Scherrer equation, where the same peak-fitting procedure was applied to all samples after background subtraction,  $K\alpha_2$  stripping, and smoothing of the diffraction patterns using X'Pert HighScore. Several well-resolved reflections were used to calculate the crystallite sizes and construct the size distribution histograms.

The XRD refinement further confirmed the coexistence of two crystalline phases in the alloys, namely the Austenite phase and the Martensite phase. Quantitative phase analysis based on the fitted peak intensities showed that the martensite fraction was approximately 51.74% for sample S1 and 60.19% for sample S5, indicating that the applied pressure conditions influence the phase balance in the alloy. The presence of the austenite phase, although smaller than the martensite phase, remains significant and contributes to the overall diffraction pattern.

The average crystallite sizes obtained for the samples were S1: 12 nm, S2: 12 nm, S3: 12 nm, S4: 6 nm, and S5: 14 nm. Since the crystallites are smaller than 100 nm, they cannot be directly observed using optical microscopy and are generally below the reliable crystallite-resolution limit of conventional scanning electron microscopy. In samples S1, S2, and S3, the distributions are relatively broad and the deviations from the mean value are larger, which may indicate heterogeneous nucleation and growth conditions. In contrast, sample S4 exhibits a narrower distribution concentrated at smaller crystallite sizes, suggesting a more homogeneous and refined

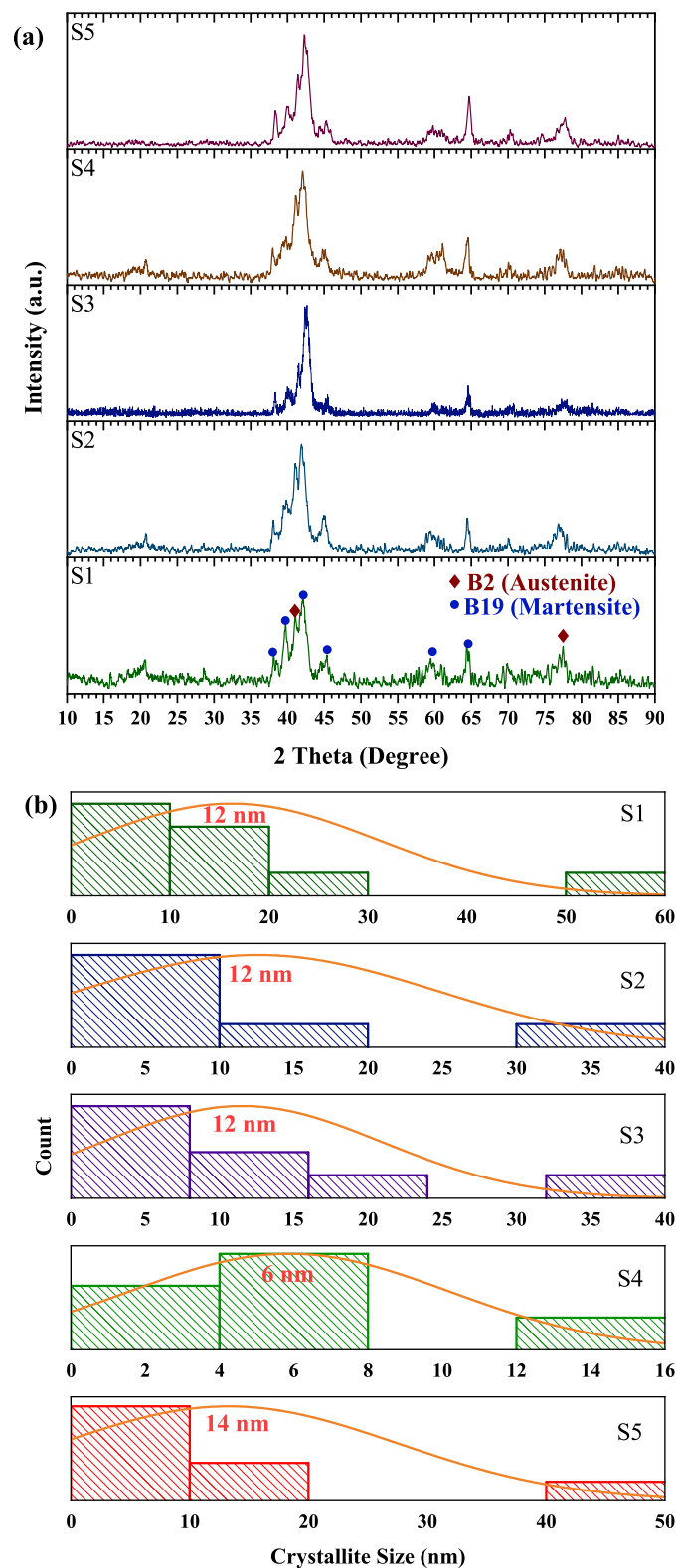


**Figure 1.** (a) The XRD pattern for various pressures, (b) The crystallite size of the alloys.

microstructure. Sample S5 shows a larger mean crystallite size together with a broader distribution, which may indicate enhanced crystallite growth under the corresponding pressure conditions.

It was observed that sample S4 (synthesized under 300 MPa pressure) exhibits the smallest crystallite size among all samples, indicating that high pressure suppresses crystallite growth and promotes grain refinement. Overall, the results show that the crystallite size and phase distribution of the alloy are strongly influenced by the applied high pressure during synthesis. These results highlight that controlling crystallite size and phase composition is crucial in the synthesis process, as narrower size

distributions and smaller crystallites are generally associated with more homogeneous and structurally stable materials.

In figure 2(a), the microstructural properties of the samples produced at different pressing pressures were examined by scanning electron microscope (SEM), and the results of surface composition analysis by energy dispersive spectroscopy (EDS) are given in figure 2(b). SEM images clearly reveal the effects of increasing pressing pressure on the sample surface morphology: accordingly, for the SEM image of the S1 (0 MPa) alloy: This sample, which has not been subjected to any pressing process, has a very irregular and porous structure. The bonding between the particles is weak and compaction after sintering has not been achieved. S2 (100 MPa): The porosity rate has decreased significantly with the applied pressure, a more compact and homogeneous structure has been obtained. The contact between the particles has increased and the sintering quality has relatively improved. S3 (200 MPa): In this sample, the density has increased and the pores in the microstructure have largely disappeared. The particles are better bonded to each other, and a tighter and more solid structure has emerged. S4 (300 MPa): The microstructure has reached maximum compactness. The amount of pores has decreased to a minimum, and the structure appears to be completely integrated. This pressure level may have provided the most suitable sintering behavior. S5 (400 MPa): Excessive pressure application has led to structural deterioration. Large-sized pores and crack-like structures have been observed. This situation can be explained by particle deformation caused by high pressure or the spring back effect [21]. EDS analyses were performed simultaneously with SEM imaging to examine the distribution of elements on the surface. Nickel (Ni), Titanium (Ti), Silver (Ag) and Copper (Cu) were detected as the main elements in all samples. The elemental compositions were generally consistent with the target composition. EDS results show that the elemental ratios do not change significantly despite the increase in pressing pressure. This reveals that the production process is controlled in terms of preserving the chemical composition. However, the differences in microstructure will be decisive on the mechanical performance. The increase in pressing pressure provides direct improvement in microstructural integrity and sintering quality. Especially in the range of 200–300 MPa, pores were minimized and a compact structure was obtained. However, at excessive pressure levels such as 400 MPa, pore formation and structural deterioration occurred again. In EDS analyses, it was seen that the elemental composition remained stable, which supported the homogeneity of the production process. These results highlight the critical role of pressing pressure in multicomponent systems produced by powder metallurgy. Pressing pressure should be carefully selected to optimize mechanical and structural properties.

In figure 3, mapped Scanning Electron Microscope (SEM) images of alloy samples obtained under different applied isostatic pressure conditions are presented. These images allow the evaluation of changes in the microstructure of the alloy together with elemental distribution maps. The colored areas in the images represent the densities of different elements and provide information about microstructural features such as homogeneity of the structure, phase distribution and porosity. For sample S1; In the reference sample produced without any pressure, an irregular and heterogeneous microstructure in terms of density is observed. The porosity ratio is relatively higher. There are scattered and segregation tendencies in the elemental distribution. This structure is an indication that it may exhibit a weak behavior in terms of mechanical properties [22]. For sample S2, it is observed that a more compact and tight structure is formed in the microstructure with the application of pressure. It is noticed that the porosity decreases and the spaces between the grains are less pronounced. The more homogeneous distribution of the elements indicates that microsegregation decreases [23]. This situation suggests that the mechanical strength starts to increase and a more controlled structure is obtained. If S3 - 200 MPa is examined; With the increase in pressure, a distinct orientation and band structures have formed in the microstructure. This probably indicates oriented recrystallization zones during deformation. At the same time, finely structured and regularly distributed second phase particles are seen. This structure shows that phase separation is controlled and a certain texture has begun to develop. S4 - 300 MPa: if examined; the structure has become quite complex. Different phases can be clearly distinguished; in some regions the microstructure is dense, in some regions there is irregular structuring and dense voids. In the elemental maps, regions with a tendency to segregation are revealed. This shows that high pressure can trigger the formation of heterogeneous phases by causing microstructural stresses in some regions [24]. Finally, S5 - 400 MPa: Under extreme pressure conditions, large pores and irregular voids have formed in the structure. The clarity of grain boundaries has decreased, phase precipitation and voids have become dominant in some regions. This structure may have negative consequences in terms of the mechanical and thermal stability of the material. It is understood that when the pressure exceeds a critical threshold, it leads the microstructure to deterioration and loose phase separation.

These SEM images show that the applied pressure seriously affects the microstructure. Low and medium pressure applications (S2-S3) increased the density and integrity of the structure by reducing porosity and providing a more homogeneous distribution of elements. However, at high pressure levels (S4-S5), undesirable structures such as phase separation, increased porosity and segregation occurred in the microstructure. This shows that the optimum pressure value is critical in the production process and must be carefully controlled to maintain structural integrity.

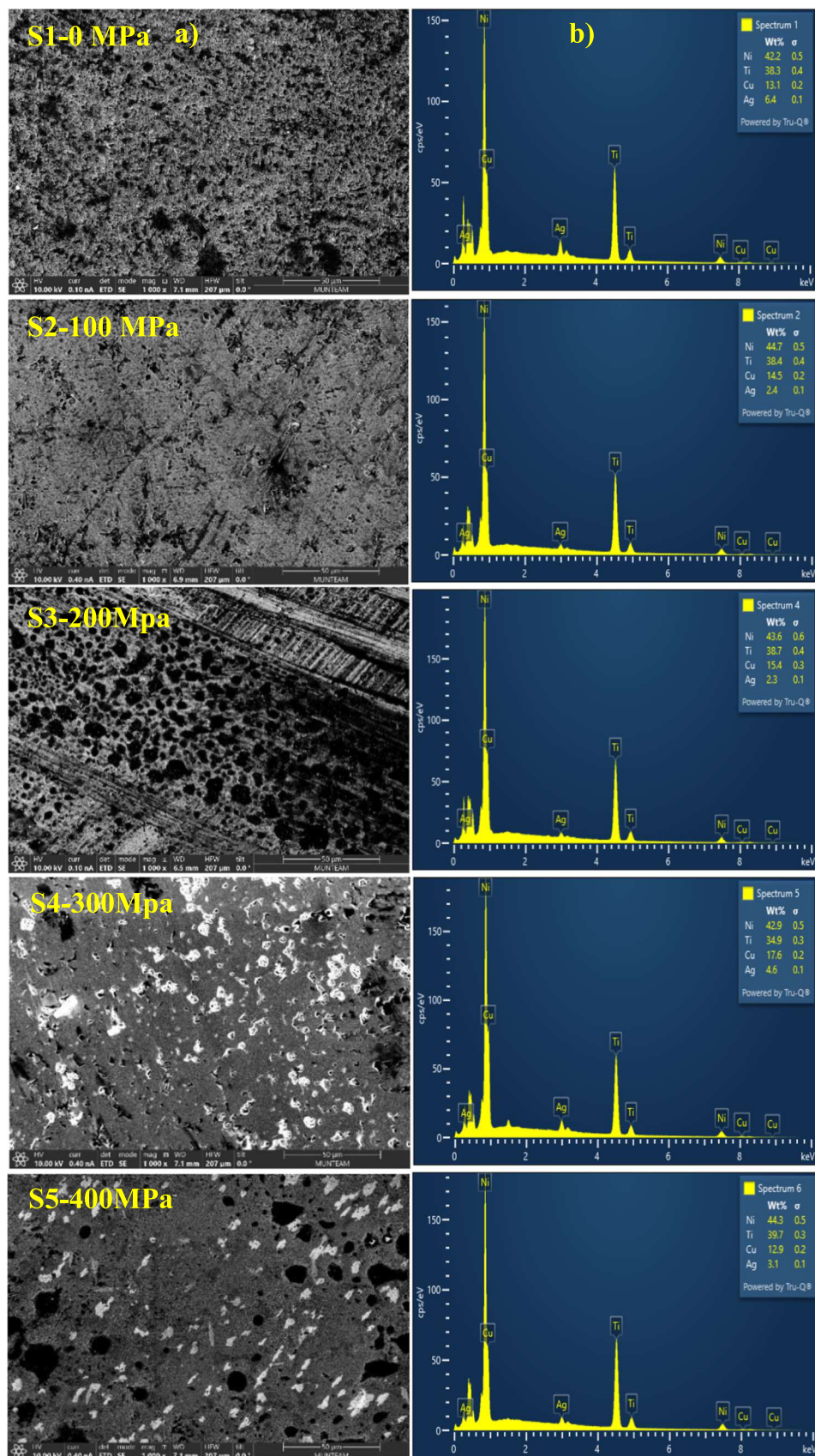


Figure 2. (a) The SEM images, (b) EDX results of all samples.

The differential scanning calorimetry (DSC) plot is used to study the phase transformations that a material undergoes under temperature change and the heat absorbed or released during these transformations. Figure 4 shows the DSC (Differential Scanning Calorimetry) curves of samples obtained under different applied



**Figure 3.** Mapping SEM images of alloys.

pressure levels. When the curves are examined, characteristic phase transitions are clearly observed for each sample. Endothermic and exothermic peaks occurring during the heating and cooling cycles represent the martensite  $\rightarrow$  austenite and austenite  $\rightarrow$  martensite transformations, respectively [25, 26]. The starting and ending

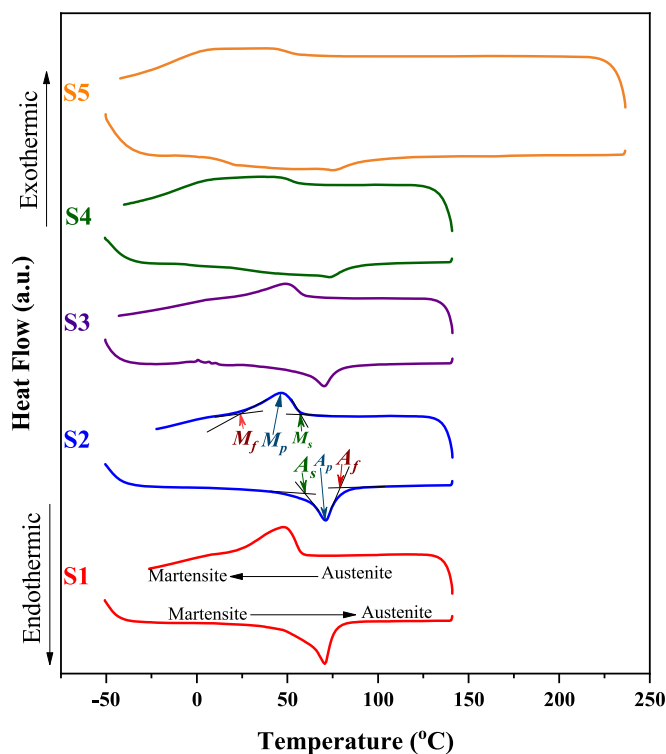


Figure 4. The DSC pattern as a function of applied pressure.

Table 1. Some physical parameters of the alloy determined with the help of DSC analysis.

| Sample | Pressure (MPa) | $M_s$ (°C) | $M_p$ (°C) | $M_f$ (°C) | $A_s$ (°C) | $A_p$ (°C) | $A_f$ (°C) | $T_o$ (°C) | Temperature hysteresis (°C) |
|--------|----------------|------------|------------|------------|------------|------------|------------|------------|-----------------------------|
| S1     | 0              | 58.5       | 47.4       | 18.9       | 43.2       | 70.6       | 77.8       | 68.1       | 24.3                        |
| S2     | 100            | 59.8       | 46.6       | 15.3       | 33.4       | 70.8       | 82.3       | 71.2       | 18.1                        |
| S3     | 200            | 63.9       | 48.8       | 21.1       | 44.5       | 70.1       | 81.4       | 72.8       | 23.4                        |
| S4     | 300            | 60.4       | 27.7       | −4.3       | 45.8       | 73.2       | 90.9       | 75.6       | 48.1                        |
| S5     | 400            | 64.2       | 42.02      | −4.9       | 49.5       | 75.6       | 96.6       | 80.4       | 54.4                        |

temperatures ( $M_s$ ,  $M_p$ ,  $A_s$ ,  $A_p$ ) corresponding to these transformations are marked on each sample [27–29]. The obtained data reveal that the applied pressure has a significant effect on the phase transition temperatures. While the martensite transformation occurs at lower temperatures under low pressure (S1), it is observed that these transformation temperatures shift generally upwards as the applied pressure increases (S2–S5). Additionally, it has been observed that the transition temperature range between the austenite phase and the martensite phase occurs over a wider range as the applied pressure increases. This situation may be related to pressure affecting the atomic-level order, thereby influencing the crystal structure and consequently altering the thermodynamic stability and transformation temperatures of the martensite phase [30]. Thus, when examining the shape and area of endothermic and exothermic peaks in DSC curves, it is observed that the enthalpies of transformation are also affected by pressure. The expansion observed in peak areas as pressure increases indicates a decrease in the amount of heat absorbed or released during transformation. This may be an indicator of changes in transformation kinetics. In this context, the controllability of transformation temperatures enables the functional customization of the alloy in pressure-sensitive applications—such as actuator systems, sensors, or thermomechanical memory elements. [31]. Table 1 shows some physical parameters of the alloy determined by DSC analysis. The equilibrium temperature at which the Gibbs free energies of martensite and austenite are equal is expressed as ' $T_o$ '; it is calculated by summing the martensite start ( $M_s$ ) and austenite end ( $A_f$ ) temperatures and taking the average [32–34]. There is a significant decrease in temperature at the  $M_f$  point. This indicates that transformation to the martensitic phase is more difficult under high pressure. The dramatic decrease at  $M_f$  shows that the temperature required for the martensitic phase to complete is highly sensitive to pressure. The austenite transformation temperature and the martensite transformation temperature increase regularly with pressure. This indicates that the transformation to the austenite phase begins and completes over a wider

**Table 2.** Thermal analysis parameters derived from DSC measurements of alloys exposed to varying pressure conditions.

| Pressure (MPa) | $\Delta H^{M \rightarrow A}$ (J.g <sup>-1</sup> ) | $\Delta H^{A \rightarrow M}$ (J.g <sup>-1</sup> ) | $\Delta S^{M \rightarrow A}$ (J(g.°C) <sup>-1</sup> ) | $\Delta G^{M \rightarrow A}$ (J/g) | $\Delta E_e$ (J/g) | $\varepsilon^{M-P}$ (%) |
|----------------|---------------------------------------------------|---------------------------------------------------|-------------------------------------------------------|------------------------------------|--------------------|-------------------------|
| 0              | 19.7                                              | 16                                                | 0.289                                                 | 2.777                              | 11.456             | —                       |
| 100            | 16.7                                              | 12                                                | 0.234                                                 | 2.673                              | 10.413             | 0.158                   |
| 200            | 12.4                                              | 10.1                                              | 0.170                                                 | 1.515                              | 7.276              | 0.010                   |
| 300            | 14.8                                              | 13.2                                              | 0.195                                                 | 2.974                              | 12.616             | 0.013                   |
| 400            | 15.5                                              | 14                                                | 0.192                                                 | 3.123                              | 13.267             | 0.025                   |

temperature range, meaning that the martensite phase becomes more stable with increasing pressure. The  $T_o$  value in the data increases slightly with pressure: S1: 68.1 °C  $\rightarrow$  S5: 80.4 °C; this shows that the overall transformation temperature shifts to higher values under high pressure. Several key thermodynamic parameters were calculated based on the heat flow data recorded during phase transitions. One of these is the enthalpy change ( $\Delta H$ ) from thermodynamic values. Since the alloy exhibits phase transformations, the heat absorbed or released can be determined by the equation (2) [35], which can be used to calculate  $\Delta H$ . This parameter is fundamental in evaluating the energy required to overcome the structural rearrangement associated with phase changes:

$$\Delta H^{M \rightarrow A} = \int_{A_s}^{A_f} \frac{dq}{dt} \left( \frac{dT}{dt} \right)^{-1} dT \quad (2)$$

here  $T$  represents absolute temperature and  $t$  represents time. Entropy ( $\Delta S$ ) can be defined as another physical parameter of alloys that can change during a thermodynamic process [36]. Entropy can be found with the help of equation (3) [37, 38]:

$$\Delta S^{M \rightarrow A} = \frac{\Delta H^{M \rightarrow A}}{T_o} \quad (3)$$

here  $T_o$  is the equilibrium temperature, as previously defined in the text. The Gibbs free energy ( $G$ ) value varies proportionally with temperature. Moreover, the Gibbs free energy change ( $\Delta G$ ) which provides information about the spontaneity and thermodynamic favorability of the phase transformation and elastic energy  $\Delta E_e$  stored in the self-accommodated martensitic variants can be calculated at specific transformation temperatures using equations (4), (5): [39, 40]

$$\Delta G^{M \rightarrow A}(M_s) = -(T_o - M_s) \Delta S^{M \rightarrow A} \quad (4)$$

$$\Delta E_e^{M \rightarrow A} = (M_s - M_f) \Delta S^{M \rightarrow A} \quad (5)$$

In materials such as shape memory alloys, there is often a temperature difference (such as  $\Delta T = A_s - M_f$ ) during the martensite  $\leftrightarrow$  austenite transformation [41]. This difference is called thermal hysteresis ( $H$ ). It is known in the literature that hysteresis in martensitic transformations that occur depending on temperature is closely related to the composition of the alloy [42]. However, the relationship between pressure and the  $A_s$ ,  $A_f$  transformation temperatures for the alloy can be expressed using the Clausius–Clapeyron equation [34].

$$\frac{d(A_s)}{d\sigma} \approx \frac{\varepsilon^{M-A} A_s(\sigma)}{\rho \Delta H^{M-A}(\sigma)} \quad (6)$$

In this equation,  $\varepsilon^{M-A}$  is the temperature-dependent stress,  $\sigma$  is the applied pressure,  $\rho$  is the density of the alloy, and  $\Delta H^{M-A}$  is the enthalpy change during the martensite-to-austenite transformation. From this, the approximate value of  $\varepsilon^{M-A}$  was calculated using the following equation [34, 43]:

$$\varepsilon^{M-A}(\%) = 1.61 \frac{A_s(^{\circ}\text{C}) - A_{s0}(^{\circ}\text{C})}{\sigma(\text{Mpa})} \quad (7)$$

In this equation,  $A_s(^{\circ}\text{C})$  is the austenite start temperature of the pressure-applied sample,  $A_{s0}(^{\circ}\text{C})$  is the austenite start temperature of the non-pressure-applied alloy, and  $\sigma$  is the applied pressure value in MPa [34, 43]. To better illustrate the effect of applied pressure on thermal and thermodynamic behavior, the calculated parameters derived from the DSC curves are tabulated in table 2. Accordingly, interpretation of these results sheds light on the fundamental mechanisms driving phase behavior under varying pressure conditions, as detailed below. These parameters include forward (martensite  $\rightarrow$  austenite) and reverse (austenite  $\rightarrow$  martensite) transformation enthalpies ( $\Delta H^{M \rightarrow A}$  and  $\Delta H^{A \rightarrow M}$ ), entropy change ( $\Delta S^{M \rightarrow A}$ ), free energy change ( $\Delta G^{M \rightarrow A}$ ), elastic energy difference ( $\Delta E_e$ ), and temperature hysteresis ( $H$ ). These values are critical for determining how the alloy's phase transformation behavior responds to pressure. While the  $\Delta H^{M \rightarrow A}$  value is 19.7 J.g<sup>-1</sup> at 0 MPa, it generally decreases with increasing pressure, reaching a minimum value of 12.4 J.g<sup>-1</sup> at 200 MPa. This indicates that the martensite to austenite transformation requires less energy under high pressure.

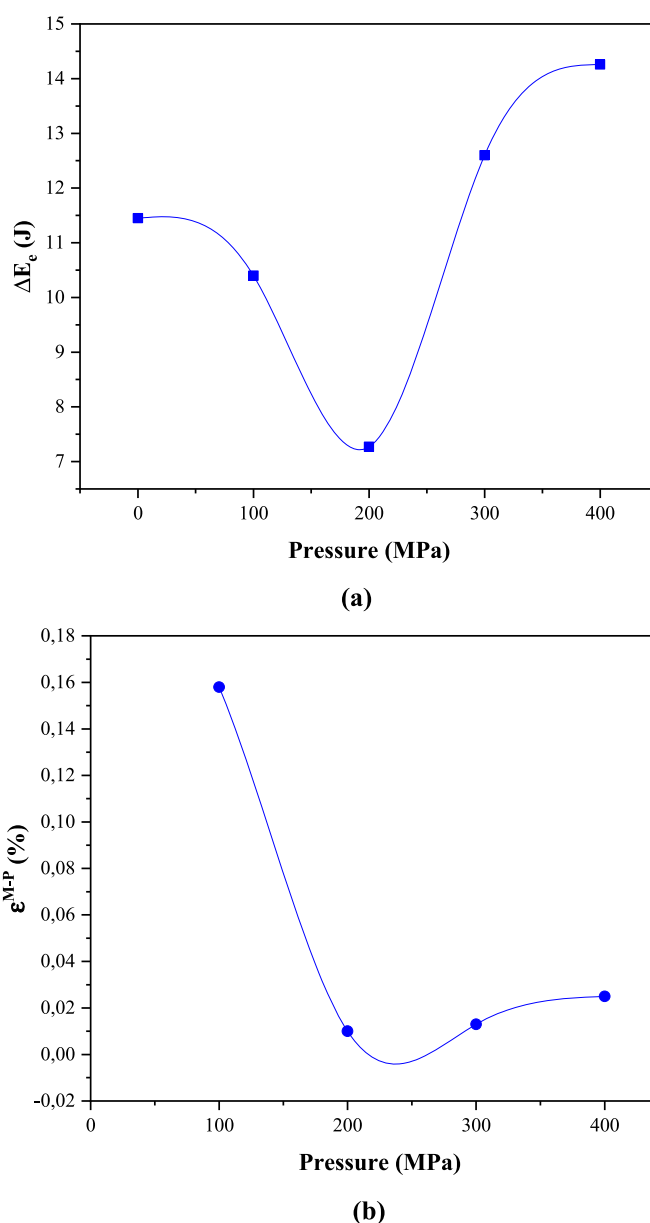


**Figure 5.** (a). The variation of the elastic energy of samples with applied pressure. (b). The variation of the strain of samples with applied pressure.

However, a slight increase in enthalpy values is observed at 300 and 400 MPa (14.8 and 15.5 J·g<sup>-1</sup>, respectively), suggesting that an increase in enthalpy may occur due to structural rearrangements at high pressure.  $\Delta H^{A \rightarrow M}$  values follow a similar trend, decreasing from 16 J·g<sup>-1</sup> at 0 MPa to 10.1 J·g<sup>-1</sup> at 200 MPa, and then increasing again to 14 J·g<sup>-1</sup> at 400 MPa. This indicates that forward and reverse recycling processes respond differently to pressure and that the transformation mechanisms are pressure sensitive.

The entropy change reflects changes in the disorder of the system. The  $\Delta S^{M \rightarrow A}$  value decreases significantly with pressure (from 0.289 J (g·°C)<sup>-1</sup> at 0 MPa to 0.192 J (g·°C)<sup>-1</sup> at 400 MPa). This decrease indicates that microstructural disorder decreases with pressure during the transformation and phase transitions become more orderly. The free energy change represents the thermodynamic driving force of the transformation. The  $\Delta G^{M \rightarrow A}$  value is 2.77 J at 0 MPa, then increasing to 3.123 J at 400 MPa. Accordingly, it is observed that the transformation requires more energy is required at higher pressures. This suggests that the kinetics and crystal structure of the phase transformation change under pressure.  $\Delta E_e$  represents the elastic energy accumulated or released during the transformation.  $\Delta E_e$ , which is 11.456 J at 0 MPa, decreases to 7.276 J at 200 MPa, and then increases to 12.616 J and 13.267 J at 300 and 400 MPa, respectively (figure 5(a)). This change indicates that the structure accumulates less mechanical energy at low pressures, while elastic deformation increases at higher pressures. Temperature hysteresis (H) represents the difference between the forward and reverse conversion temperatures and is important for the reversibility of phase transitions. The hysteresis value varies nonlinearly

with pressure. The hysteresis, which is 23.2 °C at 0 MPa, reaches a maximum of 54.4 °C at 400 MPa. This suggests that moderate pressures create a greater energy barrier during the conversion, while this barrier decreases relatively at higher pressures. It was observed that both the martensite to austenite ( $\Delta H^{M \rightarrow A}$ ) and austenite to martensite ( $\Delta H^{A \rightarrow M}$ ) transformation enthalpies decreased with increasing pressure, but this decrease was reversible at high pressures. The entropy change ( $\Delta S^{M \rightarrow A}$ ) and free energy change ( $\Delta G^{M \rightarrow A}$ ) values decreased in the low- to medium-pressure range and increased again at high pressure. This suggests that pressure reshapes the thermodynamics of the transformation by affecting microstructural arrangements. Parameters such as the elastic energy difference ( $\Delta E_e$ ) and temperature hysteresis revealed that the mechanical responses of the system during the transformation are sensitive to pressure. Figure 5(b) shows that as pressure increases, the internal stress percentage decreases due to the increase in the thermoelastic properties of the sample and its internal response to the applied pressure. This transformation accumulates in the form of lattice changes or distortions at the atomic level, reflecting the shape change of the crystal. Therefore, the thermoelastic martensitic transformation is both a mechanical and thermal process, and specific thermodynamic conditions explaining the effects of stress and temperature on the transformation have been defined thanks to this unique interaction [40].

## 4. Conclusion

In this study, the effects of varying uniaxial pressing pressures on the microstructural, thermal, and phase transformation behaviors of a quaternary  $\text{Ni}_{39}\text{Ti}_{49}\text{Cu}_8\text{Ag}_4$  shape memory alloy were systematically investigated. XRD analysis confirmed the presence of both B2 (austenite) and B19 (martensite) phases across all samples, with notable peak sharpening at 200 MPa, suggesting improved crystallinity. Crystallite size calculations using the Scherrer equation revealed that pressure directly influences grain refinement, with the smallest average crystallite size observed at 300 MPa, indicating a more homogeneous microstructure. SEM and EDS analyses demonstrated that moderate pressures (200–300 MPa) enhance sintering quality, reduce porosity, and result in better particle bonding and microstructural integrity. However, excessive pressure (400 MPa) led to the formation of cracks, large pores, and elemental segregation, highlighting a degradation in structural uniformity. Mapped SEM images further confirmed that optimal pressure levels promote uniform elemental distribution, while excessive compaction induces microstructural heterogeneity and phase separation. DSC analysis revealed that phase transformation temperatures ( $M_s$ ,  $M_f$ ,  $A_s$ ,  $A_f$ ) are highly sensitive to applied pressure. With increasing pressure, martensitic transformation became more difficult, while austenitic transformation temperatures increased, indicating enhanced thermodynamic stability of the martensite phase. The observed narrowing of DSC peak areas with pressure suggests a reduction in transformation enthalpies and altered transformation kinetics. A general evaluation of the parameters associated with DSC analysis reveals that increasing pressure initially facilitates phase transformation, but after a certain threshold, it leads to an increase in transformation energies and structural hysteresis. These findings demonstrate that pressure is a critical control parameter not only at the thermal but also at the structural level, providing an important basis for pressure-optimized shape memory alloy designs. Moderate pressures not only improve microstructural compactness and phase stability but also enable functional tunability of transformation behavior-making such alloys highly promising for use in advanced applications such as actuators, sensors, and biomedical devices.

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## Credit authorship contribution statement

**C. TATAR:** Supervision, Project administration, **M. KOK:** Writing—review, data analysis and writing Conceptualization. **M.S. KANCA:** Formal analysis, Investigation, Resources **I. N. QADER** and **E. BALCI:** writing—review.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability statement

No new data were created or analysed in this study.

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